Supplementary Material for "Approaching the complete-basis limit with a truncated many-body expansion"

Ryan M. Richard, Ka Un Lao, and John M. Herbert*

Department of Chemistry and Biochemistry,

The Ohio State University, Columbus, OH 43210

(Dated: November 7, 2013)

* herbert@chemistry.ohio-state.edu

In the main text we discussed eight ways to extrapolate to the complete basis set (CBS) limit. Here we tabulate the system energies, and the basis-set superposition error (BSSE) corrections for the $(H_2O)_6$ and $(H_2O)_{10}F^-$ systems. Additionally, the CBS values that we obtained using the extrapolation procedure

$$\widetilde{E}^X_{\text{B.E.}} = \left(E_{(H_20)_6} + E^{\text{relax}}\right) + \left(\mathcal{E}^{X*}\right) \tag{1}$$

are also given. See the main text for further details regarding the extrapolation procedure and for an explanation of the notation.

The data tables below provide the supersystem energies of the $(H_2O)_6$ and $(H_2O)_{10}F^-$ systems as computed using a normal MP2 calculation and with various truncated many-body approximations. As in the paper, we abbreviate the aug-cc-pVXZ basis set as aXZ, for X = D, T, and Q. The "a∞Z" value is the CBS extrapolation. Here, however, we have listed the Hartree-Fock energy and the MP2 correlation energy separately (whereas only total energies are discussed in the paper). We use the following abbreviations in the data tables.

- **Full-HF**: the Hartree-Fock energy of the supersystem.
- **Full-MP2**: the MP2 correlation energy of the supersystem.
- **2B**: either the energy or correlation energy as approximated by a two-body expansion.
- **EE-2B**: the same as the 2B quantity, but using electrostatic embedding.
- **3B**: similar to 2B but using a three-body expansion.
- **EE-3B**: an electrostatically-embedded three-body expansion.

BSSE corrections are obtained in various ways, as described in the paper. Here, we tabulate the quantity denoted as $\mathcal{E}^{X*}$ in the paper, although its Hartree-Fock and MP2 correlation components are listed separately here. The following BSSE corrections are employed.

- **Full-CP**: A full (supersystem) Boys-Bernardi counterpoise (CP) correction.
- **MBCP(2)**: Our many-body CP correction, truncated after two-body terms, which is equivalent to VMFC(2).
- **MBCP(3)**: Our many-body CP correction, truncated after three-body terms.

- **VMFC(3)**: The Valiron-Mayer function CP correction, truncated after three-body terms.

Cartesian coordinates for each cluster are provided in separate files.

---

[1] D. M. Bates and G. S. Tschumper, J. Phys. Chem. A **113**, 3555 (2009).

TABLE I: Hartree-Fock energies (in hartree) for the eight $(H_2O)_6$ isomers from Ref. 1.

Method and basis set		Isomer							
		Bag	Boat1	Boat2	Book1	Book2	Cage	Cyclic	Prism
Full-HF	aDz	-456.293221	-456.294703	-456.294781	-456.295088	-456.294445	-456.293819	-456.296227	-456.294168
	aTz	-456.405583	-456.408090	-456.408162	-456.407651	-456.406929	-456.405688	-456.409603	-456.405477
	aQz	-456.437163	-456.439740	-456.439819	-456.439248	-456.438503	-456.437246	-456.441242	-456.437010
	a∞	-456.440782	-456.444250	-456.444391	-456.443312	-456.442441	-456.441428	-456.445523	-456.440879
2B	aDz	-456.274896	-456.274302	-456.274319	-456.276943	-456.276951	-456.278532	-456.274833	-456.278870
	aTz	-456.387186	-456.387424	-456.387481	-456.389400	-456.389294	-456.390142	-456.387977	-456.390205
	aQz	-456.418748	-456.419031	-456.419104	-456.420974	-456.420853	-456.421716	-456.419571	-456.421783
	a∞z	-456.422361	-456.423541	-456.423678	-456.425033	-456.424799	-456.425953	-456.423845	-456.425690
EE-2B	aDz	-456.292271	-456.293661	-456.293589	-456.294032	-456.293549	-456.293349	-456.294900	-456.293524
	aDz	-456.404319	-456.406632	-456.406561	-456.406258	-456.405699	-456.404594	-456.407898	-456.404403
	aDz	-456.436153	-456.438317	-456.438252	-456.438027	-456.437496	-456.436456	-456.439526	-456.436236
	a∞z	-456.440057	-456.442921	-456.442916	-456.442302	-456.441693	-456.441022	-456.443853	-456.440457
3B	aDz	-456.291591	-456.292318	-456.292386	-456.293526	-456.293108	-456.293009	-456.293553	-456.293447
	aTz	-456.404078	-456.405670	-456.405748	-456.406180	-456.405622	-456.405096	-456.406907	-456.404831
	aQz	-456.435624	-456.437321	-456.437406	-456.437751	-456.437170	-456.436601	-456.438556	-456.436295
	a∞z	-456.439193	-456.441837	-456.441982	-456.441777	-456.441080	-456.440701	-456.442849	-456.440087
EE-3B	aDz	-456.292856	-456.294345	-456.294418	-456.294818	-456.294187	-456.293652	-456.295826	-456.294209
	aTz	-456.405483	-456.407842	-456.407936	-456.407635	-456.406804	-456.405784	-456.409335	-456.405703
	aQz	-456.437011	-456.439520	-456.439628	-456.439220	-456.438351	-456.437276	-456.441027	-456.437147
	a∞z	-456.440542	-456.444039	-456.444212	-456.443235	-456.442245	-456.441357	-456.445337	-456.440904

TABLE II: MP2 correlation energies (in hartree) for the eight $(H_2O)_6$ isomers from Ref. 1.

Method and basis set		Isomer							
		Bag	Boat1	Boat2	Book1	Book2	Cage	Cyclic	Prism
Full-MP2	aDz	-1.347255	-1.343272	-1.343006	-1.346556	-1.346803	-1.348597	-1.343318	-1.348657
	aTz	-1.642677	-1.638209	-1.637982	-1.641947	-1.642229	-1.644554	-1.638240	-1.644884
	aQz	-1.747262	-1.743065	-1.742840	-1.746580	-1.746824	-1.749086	-1.743138	-1.749394
	a∞z	-1.828075	-1.823541	-1.823314	-1.827243	-1.827499	-1.829681	-1.823820	-1.830345
2B	aDz	-1.347552	-1.343283	-1.343029	-1.346713	-1.346962	-1.349253	-1.343328	-1.349262
	aTz	-1.642711	-1.638131	-1.637942	-1.641921	-1.642157	-1.644739	-1.638180	-1.645009
	aQz	-1.747349	-1.742980	-1.742803	-1.746609	-1.746813	-1.749352	-1.743063	-1.749619
	a∞z	-1.828200	-1.823451	-1.823280	-1.827313	-1.827533	-1.830006	-1.823734	-1.830643
EE-2B	aDz	-1.348332	-1.343886	-1.343575	-1.347478	-1.347798	-1.350175	-1.343858	-1.350365
	aTz	-1.643113	-1.638496	-1.638248	-1.642381	-1.642653	-1.645231	-1.638495	-1.645639
	aQz	-1.747637	-1.743260	-1.743030	-1.746983	-1.747215	-1.749716	-1.743292	-1.750106
	a∞z	-1.828405	-1.823669	-1.823449	-1.827624	-1.827866	-1.830276	-1.823901	-1.831026
3B	aDz	-1.346635	-1.342752	-1.342529	-1.346072	-1.346356	-1.348096	-1.342808	-1.348149
	aTz	-1.642278	-1.637725	-1.637523	-1.641594	-1.641880	-1.644274	-1.637742	-1.644630
	aQz	-1.746935	-1.742669	-1.742468	-1.746304	-1.746547	-1.748888	-1.742714	-1.749167
	a∞z	-1.827800	-1.823209	-1.823006	-1.827024	-1.827275	-1.829543	-1.823450	-1.830138
EE-3B	aDz	-1.346669	-1.343030	-1.342791	-1.346178	-1.346431	-1.348051	-1.343110	-1.348095
	aTz	-1.642423	-1.638044	-1.637819	-1.641767	-1.642030	-1.644300	-1.638073	-1.644690
	aQz	-1.747144	-1.743012	-1.742793	-1.746519	-1.746735	-1.748990	-1.743075	-1.749311
	a∞z	-1.828056	-1.823570	-1.823352	-1.827269	-1.827490	-1.829700	-1.823833	-1.830343

TABLE III: Hartree-Fock energies (in hartree) for the ten $(H_2O)_{10}F^-$ isomers.

Method and basis set		Isomer 1	2	3	4	5	6	7	8	9	10
Full-HF	aDz	-859.988302	-860.005338	-859.973346	-859.980934	-859.960948	-859.974488	-859.985031	-859.987352	-859.959997	-859.960618
	aTz	-860.197544	-860.214158	-860.181784	-860.189162	-860.169700	-860.182489	-860.194625	-860.196914	-860.168017	-860.168445
	aQz	-860.256889	-860.273799	-860.240961	-860.248100	-860.228918	-860.241501	-860.253959	-860.256410	-860.226980	-860.227232
	a∞z	-860.243227	-860.278378	-860.210933	-860.224447	-860.195337	-860.213839	-860.241525	-860.250792	-860.195571	-860.179341
3B	aDz	-859.985083	-860.001898	-859.971157	-859.978747	-859.958316	-859.970393	-859.981723	-859.983615	-859.955301	-859.957193
	aTz	-860.194260	-860.210846	-860.179555	-860.187198	-860.167159	-860.178396	-860.191515	-860.193262	-860.163222	-860.164878
	aQz	-860.253465	-860.270373	-860.238575	-860.246063	-860.226293	-860.237270	-860.250825	-860.252644	-860.221950	-860.223486
	a∞z	-860.239681	-860.274822	-860.208405	-860.222308	-860.192619	-860.209478	-860.238338	-860.246905	-860.190336	-860.175450
EE-3B	aDz	-859.986444	-860.003501	-859.971752	-859.979174	-859.958236	-859.972561	-859.982821	-859.985127	-859.957299	-859.957793
	aTDz	-860.196371	-860.213471	-860.181268	-860.188195	-860.168310	-860.181587	-860.193636	-860.195751	-860.166769	-860.166655
	aQz	-860.256707	-860.273905	-860.240981	-860.247802	-860.228295	-860.241391	-860.253890	-860.256126	-860.226327	-860.226491
	a∞z	-860.243879	-860.279064	-860.211292	-860.224656	-860.195234	-860.214320	-860.242135	-860.251177	-860.195253	-860.179428

TABLE IV: MP2 energies (in hartree) for the ten $(H_2O)_{10}F^-$ isomers.

Method and basis set		Isomer 1	2	3	4	5	6	7	8	9	10
Full-MP2	aDz	-2.476267	-2.474568	-2.486263	-2.486098	-2.484816	-2.489055	-2.473943	-2.472964	-2.487332	-2.490510
	aTz	-3.027376	-3.026387	-3.037932	-3.036527	-3.035489	-3.040722	-3.024536	-3.024048	-3.038085	-3.040989
	aQz	-3.223036	-3.222141	-3.233545	-3.231684	-3.230933	-3.236228	-3.220447	-3.219976	-3.233512	-3.236301
	a∞z	-3.369327	-3.366117	-3.385745	-3.386043	-3.383434	-3.390740	-3.365965	-3.363706	-3.385480	-3.393626
3B	aDz	-2.473342	-2.472065	-2.483703	-2.483642	-2.481655	-2.485715	-2.471592	-2.470176	-2.484180	-2.487301
	aTz	-3.025686	-3.024846	-3.036303	-3.035269	-3.033775	-3.038776	-3.023053	-3.022155	-3.035830	-3.038722
	aQz	-3.221879	-3.221103	-3.232494	-3.230973	-3.229813	-3.234944	-3.219437	-3.218728	-3.231771	-3.234797
	a∞z	-3.368559	-3.365446	-3.385116	-3.385731	-3.382747	-3.389939	-3.365300	-3.362929	-3.384114	-3.392678
EE-3B	aDz	-2.473137	-2.471761	-2.483488	-2.483246	-2.481199	-2.485688	-2.471453	-2.470099	-2.484232	-2.486916
	aTz	-3.025303	-3.024440	-3.036133	-3.034749	-3.033422	-3.038737	-3.022861	-3.021969	-3.036036	-3.038514
	aQz	-3.221557	-3.220766	-3.232435	-3.230424	-3.229605	-3.234897	-3.219217	-3.218579	-3.232035	-3.234867
	a∞z	-3.368282	-3.365160	-3.385138	-3.385161	-3.382645	-3.389887	-3.365060	-3.362807	-3.384421	-3.392951

TABLE V: Hartree-Fock contribution to the BSSE correction (in hartree) for the eight $(H_2O)_6$ isomers from Ref. 1.

Method and basis set		Isomer							
		Bag	Boat1	Boat2	Book1	Book2	Cage	Cyclic	Prism
Full-CP	aDz	-456.242930	-456.243091	-456.243140	-456.243202	-456.243165	-456.243742	-456.242896	-456.243663
	aTz	-456.354440	-456.355276	-456.355319	-456.354886	-456.354788	-456.354993	-456.355075	-456.354626
	aQz	-456.385637	-456.386577	-456.386628	-456.386097	-456.385982	-456.386165	-456.386364	-456.385782
	a∞z	-456.397755	-456.398690	-456.398749	-456.398202	-456.398080	-456.398299	-456.398467	-456.397945
MBCP(2)	aDz	-456.242947	-456.243234	-456.243243	-456.243241	-456.243194	-456.244007	-456.243023	-456.243652
	aTz	-456.354562	-456.355344	-456.355384	-456.354993	-456.354891	-456.355114	-456.355144	-456.354716
	aQz	-456.385728	-456.386613	-456.386672	-456.386172	-456.386059	-456.386280	-456.386403	-456.385896
	a∞z	-456.397802	-456.398708	-456.398780	-456.398237	-456.398122	-456.398430	-456.398487	-456.398066
MBCP(3)	aDz	-456.242900	-456.243128	-456.243163	-456.243135	-456.243181	-456.243638	-456.242906	-456.243737
	aTz	-456.354453	-456.355276	-456.355324	-456.354890	-456.354798	-456.355032	-456.355071	-456.354694
	aQz	-456.385629	-456.386589	-456.386630	-456.386088	-456.385978	-456.386140	-456.386366	-456.385775
	a∞z	-456.397721	-456.398719	-456.398751	-456.398170	-456.398064	-456.398193	-456.398477	-456.397869
VMFC(3)	aDz	-456.242770	-456.243028	-456.243057	-456.243078	-456.243078	-456.243573	-456.242821	-456.243689
	aTz	-456.354464	-456.355257	-456.355304	-456.354901	-456.354801	-456.355050	-456.355052	-456.354702
	aQz	-456.385615	-456.386568	-456.386619	-456.386077	-456.385964	-456.386142	-456.386353	-456.385769
	a∞z	-456.397663	-456.398684	-456.398736	-456.398129	-456.398019	-456.398167	-456.398459	-456.397842

TABLE VI: MP2 contribution to the BSSE correction (in hartree) for the eight $(H_2O)_6$ isomers from Ref. 1.

Method and basis set		Isomer							
		Bag	Boat1	Boat2	Book1	Book2	Cage	Cyclic	Prism
Full-CP	aDz	-1.332705	-1.331537	-1.331464	-1.332434	-1.332501	-1.332537	-1.331790	-1.332769
	aTz	-1.622743	-1.621619	-1.621604	-1.622490	-1.622561	-1.622744	-1.621824	-1.623120
	aQz	-1.725208	-1.724443	-1.724431	-1.724990	-1.725029	-1.725089	-1.724649	-1.725430
	a∞z	-1.799980	-1.799477	-1.799467	-1.799787	-1.799803	-1.799773	-1.799683	-1.800089
MBCP(2)	aDz	-1.333832	-1.332156	-1.332038	-1.333377	-1.333532	-1.334061	-1.332360	-1.334295
	aDz	-1.623173	-1.621917	-1.621884	-1.622871	-1.622957	-1.623257	-1.622108	-1.623644
	aDz	-1.725570	-1.724682	-1.724658	-1.725331	-1.725382	-1.725515	-1.724870	-1.725880
	a∞z	-1.800292	-1.799673	-1.799655	-1.800099	-1.800125	-1.800136	-1.799858	-1.800485
MBCP(3)	aDz	-1.332236	-1.331373	-1.331325	-1.332100	-1.332162	-1.331999	-1.331680	-1.332225
	aTz	-1.622566	-1.621509	-1.621489	-1.622346	-1.622404	-1.622532	-1.621726	-1.622936
	aQz	-1.725116	-1.724415	-1.724412	-1.724933	-1.724956	-1.725003	-1.724632	-1.725313
	a∞z	-1.799950	-1.799509	-1.799518	-1.799794	-1.799791	-1.799779	-1.799726	-1.800021
VMFC(3)	aDz	-1.333001	-1.331813	-1.331760	-1.332789	-1.332896	-1.332983	-1.332097	-1.333212
	aTz	-1.622912	-1.621742	-1.621728	-1.622657	-1.622725	-1.622952	-1.621958	-1.623381
	aQz	-1.725275	-1.724529	-1.724519	-1.725076	-1.725102	-1.725182	-1.724739	-1.725507
	a∞z	-1.799972	-1.799535	-1.799528	-1.799814	-1.799810	-1.799781	-1.799742	-1.800031

TABLE VII: Hartree-Fock contribution to the BSSE corrections (in hartree) for the ten $(H_2O)_{10}F^-$ isomers.

Method and basis set		Isomer 1	2	3	4	5	6	7	8	9	10
Full-CP	aDz	-859.809215	-859.827169	-859.794436	-859.801210	-859.790502	-859.797704	-859.810486	-859.816966	-859.793633	-859.777732
	aDz	-860.018745	-860.036089	-860.002710	-860.009602	-859.999132	-860.005368	-860.019999	-860.026385	-860.001751	-859.985734
	aDz	-860.077524	-860.095128	-860.061268	-860.067970	-860.057726	-860.063796	-860.078813	-860.085357	-860.060165	-860.043927
	a∞z	-860.100442	-860.118384	-860.084172	-860.090679	-860.080609	-860.086671	-860.101767	-860.108473	-860.082958	-860.066532
MBCP(2)	aDz	-859.809031	-859.827160	-859.794265	-859.801031	-859.790263	-859.797632	-859.810182	-859.816621	-859.793325	-859.777515
	aTz	-860.018922	-860.036271	-860.002892	-860.009779	-859.999309	-860.005519	-860.020128	-860.026516	-860.001893	-859.985876
	aQz	-860.077722	-860.095333	-860.061471	-860.068165	-860.057918	-860.064014	-860.078989	-860.085557	-860.060377	-860.044145
	a∞z	-860.100605	-860.118582	-860.084339	-860.090836	-860.080753	-860.086918	-860.101922	-860.108664	-860.083167	-860.066766
MBCP(3)	aDz	-859.808933	-859.826623	-859.794144	-859.800798	-859.790030	-859.797190	-859.809949	-859.816350	-859.793034	-859.777343
	aTz	-860.018803	-860.036078	-860.002730	-860.009590	-859.999082	-860.005360	-860.019911	-860.026322	-860.001730	-859.985698
	aQz	-860.077551	-860.095125	-860.061272	-860.067969	-860.057717	-860.063788	-860.078810	-860.085335	-860.060144	-860.043912
	a∞z	-860.100389	-860.118306	-860.084113	-860.090627	-860.080574	-860.086586	-860.101775	-860.108404	-860.082849	-860.066483
VMFC(3)	aDz	-859.809755	-859.827653	-859.795085	-859.801524	-859.790898	-859.798326	-859.810652	-859.817399	-859.794536	-859.778478
	aTz	-860.019257	-860.036627	-860.003223	-860.010063	-859.999598	-860.005961	-860.020430	-860.026885	-860.002454	-859.986382
	aQz	-860.077701	-860.095310	-860.061440	-860.068113	-860.057893	-860.063976	-860.078989	-860.085521	-860.060383	-860.044157
	a∞z	-860.100314	-860.118224	-860.084047	-860.090506	-860.080489	-860.086471	-860.101665	-860.108314	-860.082757	-860.066391

TABLE VIII: MP2 contribution to the BSSE correction (in hartree) for the ten $(H_2O)_{10}F^-$ isomers.

Method and basis set		Isomer 1	2	3	4	5	6	7	8	9	10
Full-CP	aDz	-2.454273	-2.451837	-2.461951	-2.464172	-2.461933	-2.465027	-2.453141	-2.451282	-2.462448	-2.468108
	aDz	-2.996316	-2.994196	-3.003384	-3.005656	-3.003321	-3.006168	-2.994909	-2.993292	-3.003236	-3.008899
	aDz	-3.188904	-3.186651	-3.195382	-3.197709	-3.195553	-3.198035	-3.187729	-3.186057	-3.195286	-3.200792
	a∞z	-3.329441	-3.327091	-3.335489	-3.337856	-3.335830	-3.338046	-3.328435	-3.326723	-3.335431	-3.340822
MBCP(2)	aDz	-2.457624	-2.455339	-2.465492	-2.467517	-2.465158	-2.468619	-2.456083	-2.454610	-2.465906	-2.471534
	aDz	-2.998131	-2.996064	-3.005147	-3.007409	-3.005029	-3.007927	-2.996526	-2.995037	-3.005153	-3.010782
	aDz	-3.190120	-3.187912	-3.196580	-3.198862	-3.196654	-3.199312	-3.188860	-3.187274	-3.196587	-3.202046
	a∞z	-3.330220	-3.327910	-3.336275	-3.338571	-3.336488	-3.338971	-3.329212	-3.327556	-3.336282	-3.341617
MBCP(3)	aDz	-2.451570	-2.449281	-2.459408	-2.461497	-2.459067	-2.461917	-2.450849	-2.448649	-2.459815	-2.465208
	aDz	-2.994918	-2.992787	-3.001954	-3.004279	-3.001912	-3.004579	-2.993592	-2.991685	-3.001678	-3.007174
	aDz	-3.187948	-3.185686	-3.194523	-3.196817	-3.194666	-3.197021	-3.186810	-3.185027	-3.194219	-3.199821
	a∞z	-3.328808	-3.326450	-3.335046	-3.337318	-3.335324	-3.337452	-3.327807	-3.326114	-3.334722	-3.340401
VMFC(3)	aDz	-2.448912	-2.445999	-2.456154	-2.458838	-2.456143	-2.458960	-2.447843	-2.445462	-2.456488	-2.462094
	aTz	-2.995266	-2.993167	-3.002460	-3.004683	-3.002309	-3.005099	-2.993999	-2.992128	-3.002314	-3.007639
	aQz	-3.187976	-3.185720	-3.194640	-3.196888	-3.194743	-3.197141	-3.186911	-3.185110	-3.194363	-3.199924
	a∞z	-3.328603	-3.326231	-3.334880	-3.337146	-3.335167	-3.337280	-3.327684	-3.325935	-3.334506	-3.340240